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THE TERNARY SYSTEM CaO-MgO-SiO_2

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A number of investigations dealing with one or more of the four oxides, lime, alumina, magnesia and silica, have in recent years been carried out at the Geophysical Laboratory of the Carnegie Institution of Washington, as a preliminary step in the study of the rocks and minerals of the earth's crust. These studies[1] include all of the possible binary systems and three of the four possible ternary systems which may be constructed from these oxides. The fourth ternary system has been studied only in part. We desire in this paper to present a summary of the results we have obtained in a study of the remainder of this fourth ternary system, and also to correlate these results with the results previously obtained.

The experimental methods employed are similar to the methods used in the previous investigations at this laboratory. Samples of known compositions were prepared by fusing together in platinum crucibles weighed amounts of chemically pure calcium carbonate, magnesia and silica and subsequently reducing the samples to fine powders. The production of homogeneous samples usually necessitated the repeating of this process once or twice. The investigation of a sample was conducted as follows: a small quantity of the sample was wrapped in a piece of platinum foil which was about 1 sq. cm. in area and this charge was tied by a fine platinum wire to a small ring of marquardt porcelain. The porcelain ring was hung on a fine platinum wire, the ends of which were connected to two stout platinum leads. A marquardt porcelain tube carried these leads and also a platinum-platinrhodium thermoelement the junction of which was not more than a few millimeters from the charge. The charge, thermoelement, etc., were inserted into a hot platinum resistance furnace and the furnace temperature was regulated in such a manner as to maintain the charge at a predetermined temperature for a sufficient time to allow an equilibrium condition to be attained (usually from fifteen to thirty minutes but sometimes as long as forty-eight hours). The wire supporting the ring and the charge was then fused by passing an electric current through it, and the charge fell into a mercury bath which instantly chilled it. When cold the charge was opened and the content was examined under a petrographic microscope by means of which the phases present could be identified.

The results of the hundreds of heat treatments which were carried out during this study cannot be presented in detail in a paper as brief as this one must be, but we hope in a general way to indicate their character.

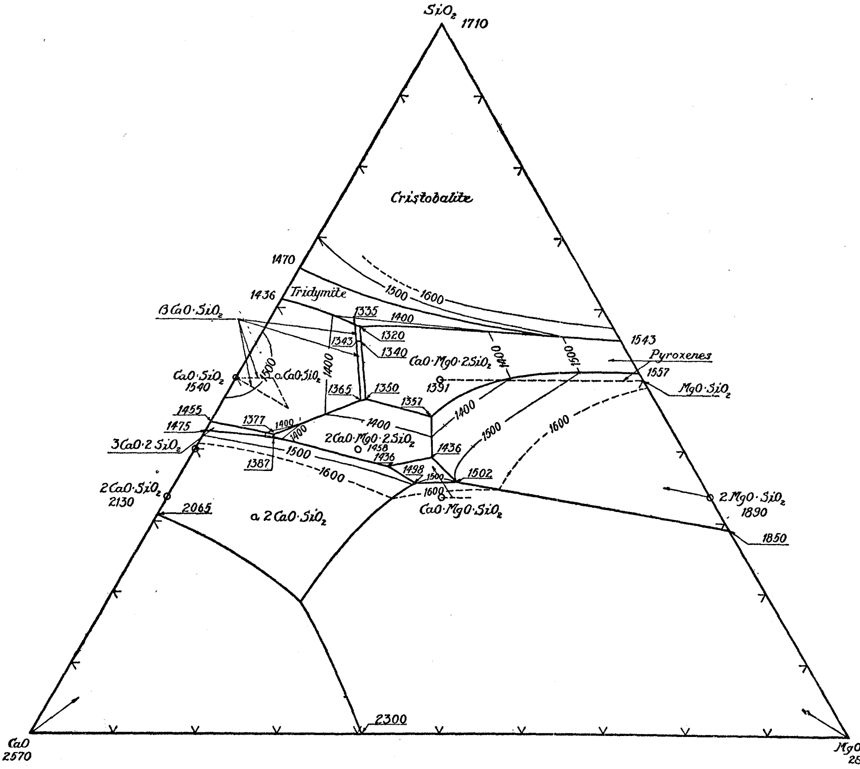

FIG. 1. THE TRIANGULAR CONCENTRATION DIAGRAM IN MOL-PER CENT

The heavy lines are the boundaries of the fields, the solid light lines are the isotherms which are readily measured, the lighter dotted lines are the high temperature isotherms which are not so accurately known and the heavier dotted lines are limits of the solid solutions. The solid solutions may also be distinguished from the isotherms in that they have arrows which indicate the fields which correspond to the respective solid solutions. The temperatures given correspond to (1) the quintuple points, (2) the quadruple points, (3) the melting points of the compounds and (4) the melting points of the component oxides.

The phases which occur in the three main binary systems and which also have fields in the ternary system are: (1) Cristobalite, SiO_2, (2) Tridymite, SiO_2, (3) Pseudowollastonite, α $CaO.SiO_2$, (4) Tricalcium di-silicate, $3CaO.2SiO_2$, (5) α Calcium orthosilicate, α $2CaO.SiO_2$, (6) Lime, CaO, (7) Periclase, MgO, (8) Forsterite, $2MgO.SiO_2$.

The binary compounds which do not have fields in the ternary system are: (1) Tricalcium silicate, $3CaO.SiO_2$, (2) Clino-enstatite, $MgO.SiO_2$.

The ternary compounds which have fields in the ternary system are: (1) Diopside, $CaO.MgO.2SiO_2$, (2) $2CaO.MgO.2SiO_2$.

The additional phases which have fields in the ternary system are not of constant composition but are ternary in character. They are:

1. The wollastonite ($\beta CaO.SiO_2$) solid solutions. These consist of either two series of solid solutions or an area of solid solution. The one series may contain up to 18 mols. per cent of diopside, $CaO.MgO.2SiO_2$ and the other up to 44 mols. per cent of the compound $2CaO.MgO.2SiO_2$. If an area of solid solution exists, it will probably extend from the one series to the other forming a triangular area with the apex at the $CaO.SiO_2$ composition. The wollastonite-pseudowollastonite inversion, $\beta CaO.SiO_2 \rightleftarrows \alpha CaO.SiO_2$ normally occurs at 1200°C. but this inversion temperature is raised by the addition of the dissolved substances reaching a maximum of 1343°C. with the diopside series and of 1365°C. with the $2CaO.MgO.2SiO_2$ series. Only those solid solutions which invert at the higher temperatures occur as primary phases since the liquidus at no point falls below 1320°C.

2. The pyroxene solid solutions which form a continuous series with end members, diopside, $CaO.MgO.2SiO_2$ and clino-enstatite, $MgO.SiO_2$, all occur as primary phases.

3. The monticellite ($CaO.MgO.SiO_2$) solid solutions which may contain up to 11% of forsterite, $2MgO.SiO_2$, are partly represented as primary phases. The pure compound monticellite probably does not occur, as a phase, stable in contact with a liquid.

Of the phases which have just been enumerated the $\beta CaO.SiO_2 - 2CaO.MgO.2SiO_2$ solid solutions, and the compound $2CaO.MgO.2SiO_2$ have not been previously noted. This latter compound has practically identical optical properties with the mineral åkermanite for which the formula $8CaO.4MgO.9SiO_2$ has been proposed, by Schaller.[2]

The summarized temperature and concentration relations are shown in figure 1. The compositions are herein represented on an equilateral triangle in mol-per cent, and the diagram includes (1) the location of the fields, with their boundary curves, (2) the location of the invariant points, (3) the temperatures which correspond to the fixed points, and (4) the isotherms which indicate the slopes which the various fields have on a solid model upon which the temperatures of complete melting are represented as vertical distances above a triangular concentration diagram similar to the one shown.

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